# Electronic Structure of Octacyanides of Molybdenum IV and V According to the SCCC MO Method. The $D_{2d}$ Case

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The electronic structure of dodecahedral octacyanides of molybdenum IV and V is described in terms of SCCC molecular orbitals. Five MO's resemble d orbitals of the central atom. The splitting of appropriate levels is almost exactly the same as that following from the crystal field theory for $G_4/G_2 \sim 0.7$. According to the theory stable $Mo(CN)_8{}^{4-}$ is dodecahedral and stable $Mo(CN)_8{}^{3-}$ is antiprismatic. In the dodecahedron the A-type ligands are bonded more strongly than the B-type ligands.

## 1. Introduction

The structure of octacyanides of molybdenum IV and V has been the subject of analysis for many years. Two conformations have been considered, one having $D_{4d}$ and the other $D_{2d}$ symmetry. Let us start with a short review.

According to X-ray analysis $Mo(CN)_8{}^{4-}$ is dodecahedral[1]. On the other hand, in $Cd_2[Mo(CN)_8(N_2H_4)_2] \cdot 4\,H_2O$, a product of a photoreaction, the anion, is antiprismatic[2]. The structure of $Mo(CN)_8{}^{3-}$ is still disputable. The isomorphous $W(CN)_8{}^{3-}$ is said to be antiprismatic[3]. However, a low symmetry of the cation can lower the symmetry of the anion. Thus it is no wonder that in tris(tetra-n-butylammonium)octacyanomolybdate (V) the anion has the shape of a dodecahedron deformed towards that of an antiprism[4].

Other experimental work is concerned with the IR and the Raman spectra. Historically, a first full analysis was carried out by STAMMREICH and SALA[5]. It followed from their analysis of the Raman spectrum of aqueous solutions and the IR spectrum of solid samples that $Mo(CN)_8{}^{4-}$ should be antiprismatic. A different conclusion was drawn by Parish from the analysis of the IR spectrum of several $Me_4W(CN)_8 \cdot x\,H_2O$ salts[6]. In the last few years three other fine papers on the subject have been published[7–9]. In contrast to the previous works, both the Raman spectrum and the IR spectrum have been measured and discussed separately for the solid state and for solutions. The conclusion was drawn that both $Mo(CN)_8{}^{4-}$ and $W(CN)_8{}^{4-}$ are antiprismatic in water and dodecahedral in the dihydrate salts. Let us recall, however, that LONG and VERNON draw a different conclusions[10]. Analyzing the Laser-Raman depolarization ratios they have been forced to assume that the dodecahedral structure of $Mo(CN)_8{}^{4-}$ and $W(CN)_8{}^{4-}$ in the crystalline environment is also maintained in water.

In the case of $Mo(CN)_8{}^{3-}$ and $W(CN)_8{}^{3-}$ the application of the EPR method is possible. Most extensive seems to be the analysis of the EPR spectrum carried out by MCGARVEY[11]. He considered also the spectrum of these paramagnetic anions when trapped in the crystal lattice of $K_4Mo(CN)_8$ and $K_4W(CN)_8$ samples respectively. According to McGarvey $Mo(CN)_8{}^{3-}$ should be an antiprismatic (in solution) and $Mo(CN)_8{}^{4-}$ dodecahedral (in the crystal).

The analysis of the NMR spectrum is so far inconclusive. According to Muetterties there is most likely a rapid intramolecular exchange of cyanide groups and a non-rigid structure[12].

The earlier theoretical work was mainly concerned with the maximum overlap principle[13–16]. DUFFEY[13] and RACAH[14] restricted the discussion to pure $\sigma$ bonds. They predicted the antiprism to be more stable than the dodecahedron. Also inclusion of $\pi$-bonding effects leads to this conclusion[16]. Another approach is based on minimization of the ligand-ligand repulsion energy[17, 18]. It follows from these papers that a fluctuating structure is most likely with a barrier smaller than 1 kcal/mole.

All remaining theoretical treatments deal with the discussion of the electronic absorption spectrum. A splitting of d levels in the $D_{2d}$ crystal field was discussed by RANDIĆ[19]. More complete was the interpretation of the spectrum given by GOLDING and

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CARRINGTON[20]. However, their analysis seems to contain some errors. The dodecahedral crystal field was also the basis of the approach given by M. BASU and S. BASU[21]. These authors did not consider the results obtained by other authors. A crystal field of the $D_{4d}$ symmetry was discussed by GLIEMANN[22] and KÖNIG[23]. Their model was later refined allowing for a flattening of the antiprism[24]. A ligand field theory for a field of an intermediate symmetry ($C_s$) was discussed by PERUMAREDDI, LIEHR and ADAMSON[25]. Surprisingly, despite so very different assumptions a good agreement with experiment was obtained in all these treatments. It is likely that differences caused by the choice of a different model have been smoothed out by the choice of a different set of empirical parameters.

A more advanced treatment is based on the SCCC MO method of BALLLHAUSEN and GRAY[26]. With a certain modification of the method an analysis was carried out already for the anions with $D_{4d}$ symmetry[27]. In contrast to all the other approaches no parameters were fitted such as to optimize the agreement with experiment. However, an analogous analysis for the case of a dodecahedron was still lacking. It is the purpose of the present work to fill up this gap.

## 2. Details of the Approach

The details of our modification of the SCCC MO method are described elsewhere[27]. Therefore we draw attention to some special points only. The population analysis is based on Löwdin's orthogonalized orbitals and not in accordance with the Mulliken population analysis. The highest occupied $\sigma$ orbital as well as $\pi$ and $\pi^*$ orbitals of the ligands are used[28]. Resonance integrals are approximated by the Wolfsberg and Helmholz formula, where $F_\sigma(\mathrm{M, L}) = 2.2$, $F_\pi(\mathrm{M, L}) = 2.0$ and $F_\sigma(\mathrm{L, L}) = F_\pi(\mathrm{L, L}) = 2.1$. As a matter of fact, a common value $F_\sigma(\mathrm{M, L}) = F_\pi(\mathrm{M, L}) = F(\mathrm{L, L}) = 2.0$ is expected to yield almost the same results. The accepted values are the same as those assumed by MANOHARAN and GRAY in their successful treatment of pentacyanonitrosyls[28] and in our preceding work[27].

All the overlap integrals were calculated exactly with the use of approximate Hartree-Fock atomic orbitals of Mo(I)[29] and SCF $\sigma$, $\pi$ and $\pi^*$ molecular orbitals of $(CN^-)$'s[28]. The calculations were performed for the following interatomic distances: $R(\mathrm{Mo-C}) = 4.080$ a. u., $R(\mathrm{C-N}) = 2.191$ a. u. The orientation of cyanide $\sigma$, $\pi$ and $\pi^*$ molecular orbitals was chosen as explained in Figure 1. From 9 metal valence oritals and 40 ligand orbitals altogether 49 molecular orbitals could be constructed. Their symmetry species are as follows: $8a_1$, $4a_2$ · $5b_1$, $8b_2$ and 12e.

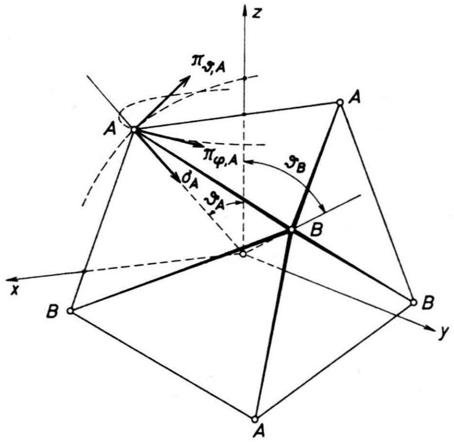

Fig. 1. A description of the dodecahedral model of octacyanides of molybdenum; in the figure a typical orientation of the $\sigma_A$, $\pi_{\vartheta A}$ and $\pi_{\varphi A}$ ligand orbitals is also shown.

Exact SCCC MO calculations were performed for the hard sphere model. In this case $\vartheta_A = 36.85°$ and $\vartheta_B = 69.46°$ (Figure 1)[17]. Approximate calculations were performed for the HOARD and NORDSIECK model[30]. Passing to the latter case, the metal-ligand overlap integrals were corrected by a Taylor expansion. A corresponding correction of ligand-ligand overlap integrals was neglected.

The program is running in Algol 60. The iteration procedure was continued until the maximum change of all the orbital energies was not greater than 0.008 kK.

## 3. Electronic Configuration

Let us assume, as customary in any one electron theory, that the sum of orbital energies of all the valence electrons ($E_{tot}$) is a relative measure of the total energy of the system. $E_{tot}$ is likely to be a useful quantity in a conformation analysis (vide many applications of the Extended Hückel Theory) provided the structures to be compared differ not too much. Thus we can compare the stability of the two dodecahedral models just considered. It was found both for the Mo(IV) and Mo(V) case that the Hoard and Nordsieck model gives a lower value of $E_{\text{tot}}$ than the hard sphere model. The difference is not large, $\Delta E_{\text{tot}} = 0.3 - 0.5$ kK. For this reason we have restricted the discussion to the experimental Hoard and Nordsieck model mainly.

The calculated orbital energies (except for states of a very high or a very low energy) are listed in Table 1 (the eigenvectors can supplied on request). In the Table we quote also those metal and ligand orbitals which give a large contribution to the appropriate molecular orbital.

Table 1. Orbital energies of $Mo(CN)_8{}^{3-}$ and $Mo(CN)_8{}^{4-}$ following from the Hoard and Nordsieck model.

| $Mo(CN)_8^{3-}$ Energy (kK) | Description of the orbital | $Mo(CN)_8^{4-}$ Energy (kK) | Description of the orbital |
|---|---|---|---|
| − 28.0 | $9\,e(\pi_\vartheta^*, \pi_\varphi^*)$ | − 27.9 | $6\,a_1(\pi_\vartheta^*)$ |
| − 29.4 | $8\,e(\pi_\varphi^*)$ | − 29.3 | $8\,e(\pi_\varphi^*)$ |
| − 29.5 | $6\,b_2(\pi_\vartheta^*)$ | − 29.6 | $6\,b_2(\pi_\vartheta^*)$ |
| − 30.6 | $3\,a_2(\pi_\varphi^*)$ | − 30.6 | $3\,a_2(\pi_\varphi^*)$ |
| − 30.9 | $4\,b_1(\pi_\varphi^*)$ | − 30.9 | $4\,b_1(\pi_\varphi^*)$ |
| − 49.3 | $5\,b_2(d_{x^2-y^2} > \sigma)$ | − 46.0 | $5\,b_2(d_{x^2-y^2} > \sigma > \pi_\vartheta^*)$ |
| − 56.4 | $7\,e(d_{xz}, d_{yz} > \sigma)$ | − 52.8 | $7\,e(d_{xz}, d_{yz} > \sigma)$ |
| − 59.3 | $5\,a_1(d_{z^2} > \sigma)$ | − 55.6 | $5\,a_1(d_{z^2} > \sigma)$ |
| − 82.6 | $3\,b_1(d_{xy})$ | − 75.7 | $3\,b_1(d_{xy})$ |
| −104.4 | $6\,e(\pi_\vartheta)$ | −103.5 | $4\,a_1(\sigma > d_{z^2})$ |
| −106.5 | $4\,a_1(\sigma > d_{z^2})$ | −104.3 | $6\,e(\pi_\vartheta > \pi_{\varphi A})$ |
| −107.0 | $5\,e(\sigma, \pi_\vartheta, \pi_\varphi)$ | −106.6 | $5\,e(\sigma > \pi_\vartheta, \pi_\varphi)$ |
| −108.2 | $2\,b_1(\pi_\varphi)$ | −106.9 | $4\,e(\sigma > \pi_\vartheta, d)$ |
| −108.6 | $4\,b_2(\pi_\vartheta > \sigma_A)$ | −108.1 | $2\,b_1(\pi_\varphi)$ |
| −109.4 | $4\,e(\sigma > d > \pi_\varphi)$ | −108.2 | $4\,b_2(\pi_\vartheta, \sigma_A)$ |
| ⋮ | ⋮ | ⋮ | ⋮ |
| −158.5 | $1\,a_1(\sigma > s)$ | −155.7 | $1\,a_1(\sigma > s)$ |

In accordance with the Table, exactly five molecular orbitals exist which resemble the molybdenum 4d orbitals. The appropriate levels correspond thus to the splitted 4d levels of the crystal field theory. Results of the Löwdin population analysis of these molecular orbitals are given in Table 2. A lowest energy has the $3b_1$ orbital with an 81 − 83% contribution from the $d_{xy}$ orbital. The contribution of $\pi$ and $\pi^*$ orbitals is small, but comparable. The other three "*d*" levels are strongly antibonding, with a relatively large contribution from the ligand $\sigma$ orbitals. The ordering of the four "*d*" levels is quantitatively the same as that following from the crystal field theory for the ratio $G_4/G_2 \gtrsim 0.5$ (Fig. 2):

$$d_{xy} < d_{z^2} < d_{xz}, d_{yz} < d_{x^2-y^2} .$$

The overall splitting increases with the oxidation state. It is equal to 29.7 kK for Mo(IV) and to 33.3 kK for Mo(V). Such a strong dependence seems to show that Perumareddi's et al. assumption of the independence of the splitting from the oxidation state [25] was rather unrealistic.

Some interesting conclusions follow from the electronic configuration. Let us consider the case of $Mo(CN)_8{}^{4-}$. In terms of the Löwdin orthogonalized orbitals one finds what follows:

$$s^{0.50}\ p^{1.02}\ d^{4.59}\ \sigma_A^{5.86}\ \sigma_B^{5.90}\ \pi_A^{15.73}\ \pi_B^{15.79}\ \pi_A^{*0.24}\ \pi_B^{*0.37} .$$

$\sigma_A$ means here the group of four $\sigma$ orbitals of the A-type ligands, $\sigma_B$ similarly of the B-type ones, etc. The starting configuration was

$$d^2\ \sigma_A^8\ \sigma_B^8\ \pi_A^{16}\ \pi_B^{16} .$$

The net charge of the central atom should thus be close to zero and the net charge of any of the $CN^-$ ligands should now be close to −1/2. B-type ligands should be slightly more negative than the A-type ones. There is a larger ligand to metal donation in the case of the A-type ligands than in the other case. Therefore, A-type ligands are ex-

Table 2. Population analysis of molecular orbitals in terms of Löwdin's orthogonalized atomic orbitals.

| Type of MO | $n$ (s) | $n$ (p) | $n$ (d) | $n$ ($\sigma_A$) | $n$ ($\sigma_B$) | $n$ ($\pi_A$) | $n$ ($\pi_B$) | $n$ ($\pi_A^*$) | $n$ ($\pi_B^*$) |
|---|---|---|---|---|---|---|---|---|---|
| $Mo(CN)^{8-}$ | | | | | | | | | |
| $5\,b_2\,(d_{x^2-y^2} > \sigma)$ | — | 0 | 0.546 | 0.057 | 0.355 | 0.004 | 0.001 | 0.029 | 0.009 |
| $7\,e\,(d_{xz}, d_{yz} > \sigma)$ | — | 0 | 0.539 | 0.291 | 0.112 | 0.006 | 0.006 | 0.023 | 0.024 |
| $5\,a_1\,(d_{z^2} > \sigma)$ | 0.001 | — | 0.518 | 0.203 | 0.207 | 0.011 | 0.008 | 0.029 | 0.023 |
| $3\,b_1\,(d_{xy})$ | — | — | 0.808 | — | — | 0.004 | 0.094 | 0.005 | 0.088 |
| $Mo(CN)^{8-}$ | | | | | | | | | |
| $5\,b_2\,(d_{x^2-y^2} > \sigma)$ | — | 0 | 0.597 | 0.049 | 0.302 | 0.004 | 0.001 | 0.036 | 0.011 |
| $7\,e\,(d_{xz}, d_{yz} > \sigma)$ | — | 0 | 0.599 | 0.240 | 0.092 | 0.006 | 0.006 | 0.028 | 0.029 |
| $5\,a_1\,(d_{z^2} > \sigma)$ | 0.001 | — | 0.586 | 0.165 | 0.168 | 0.011 | 0.007 | 0.035 | 0.028 |
| $3\,b_1\,(d_{yx})$ | — | — | 0.827 | — | — | 0.003 | 0.065 | 0.006 | 0.099 |

pected to be bonded more strongly than the B-type ones. Such a result is in agreement with the qualitative discussion given several years ago by ORGEL[31]. Comparing the populations of $\pi$ and $\pi^*$ orbitals, one notes that the CN bond should be weaker in the case of the B-type ligands than in the other case.

In the preceding work it was shown[27] that the "$d$" level splitting obtained with the SCCC MO method for the antiprism is comparable with that following from the crystal field theory. It is still better in the present case. In Fig. 2 we give the dependence of $\Delta E/G_2$ on $G_4/G_2$ in accordance with the crystal field theory. Empty circles represent the least square fit of the results of the SCCC MO method to the results of the crystal field theory. It is surprising how good the fit is. For the sake of completeness we give the optimal crystal field parameters:

$Mo(CN)_8^{4-}$

$G_2 = 26.2$ kK, $G_4 = 18.97$ kK, $G_4/G_2 = 0.724$;

$Mo(CN)_8^{3-}$

$G_2 = 31.6$ kK, $G_4 = 21.2$ kK, $G_4/G_2 = 0.672$.

These parameters refer to the Hoard and Nordsieck model.

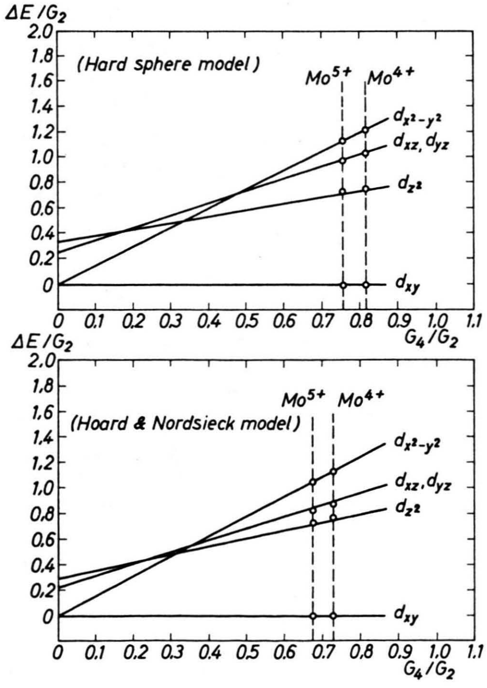

Fig. 2. Orbital energy diagrams according to the crystal field theory and a least square fit of the results of the SCCC MO method.

## 4. Relative Stability of $D_{2d}$ and $D_{4d}$ Forms

According to all the older theories the stable conformation of the anions in question should be independent of the oxidation state. The predictions of the SCCC MO method are different. Let us again assume that $E_{tot}$ is a satisfactory criterion provided the conformations to be compared differ not too much. It was shown, however, that the antiprismatic $D_{4d}$ and the dodecahedral $D_{2d}$ conformations differ not much indeed[16]. Therefore, a comparison of these two structures with respect to the total energy, $E_{tot}$, is possible. It was found that

$$E_{tot}(D_{4d}) - E_{tot}(D_{2d}) = 5.1 \text{ kK}$$

in the case of $Mo(CN)_8^{4-}$ and

$$E_{tot}(D_{4d}) - E_{tot}(D_{2d}) = -0.6 \text{ kK}$$

in the case of $Mo(CN)_8^{3-}$. This result is in a good qualitative agreement with the most recent experimental data: $Mo(CN)_8^{4-}$ should be dodecahedral and $Mo(CN)_8^{3-}$ should be antiprismatic. Admittedly, however, the difference of energies is very small in the latter case and thus the estimate is uncertain and at least a very strong vibronic coupling cannot be excluded. No doubt, however, that according to the presented analysis there is a remarkable inclination for a change of the shape of the anion with the increase of the oxidation state, from a dodecahedron towards the antiprism.

## 5. Interpretation of the Electronic Absorption Spectrum

Let us compare the experimental absorption spectrum of the two ions under consideration with the theoretical predictions which follows from the two different models of the anion. Such a comparison is given in Fig. 3 for the Mo(IV) case and in Fig. 4 for the Mo(V) case. Some explanations are necessary concerning the intensities of the predicted lines. They have been drawn more or less arbitrarily. It was assumed that allowed charge transfer bands are always stronger than the forbidden ones, forbidden charge transfer bands are always stronger than the allowed crystal field bands and that allowed crystal field bands are always stronger than the forbidden crystal field bands.

The details of our assignments are given below the figures. Instead of discussing the details we restrict the analysis to a discussion of the overall agreement with experiment. From two parts of Fig. 3 one can see immediately that for $Mo(CN)_8^{4-}$ the theoretical predictions are in favour of the $D_{2d}$ form. A different conclusion follows from the analysis of the two parts of Figure 4. Thus for $Mo(CN)_8^{3-}$ the theory is rather in favour of the $D_{4d}$ form.

To complete this analysis, let us note that there is a charge transfer to solvent bands reported in the case of octacyanides of molybdenum(IV), lying at 34 – 38 kK [32]. It might be responsible for the appearance of the band c or d (Figure 3).

Let us recall that all theoretical predictions which follow from the SCCC MO method are consistent with each other and seem to be in a qualitative agreement with most recent experimental works.

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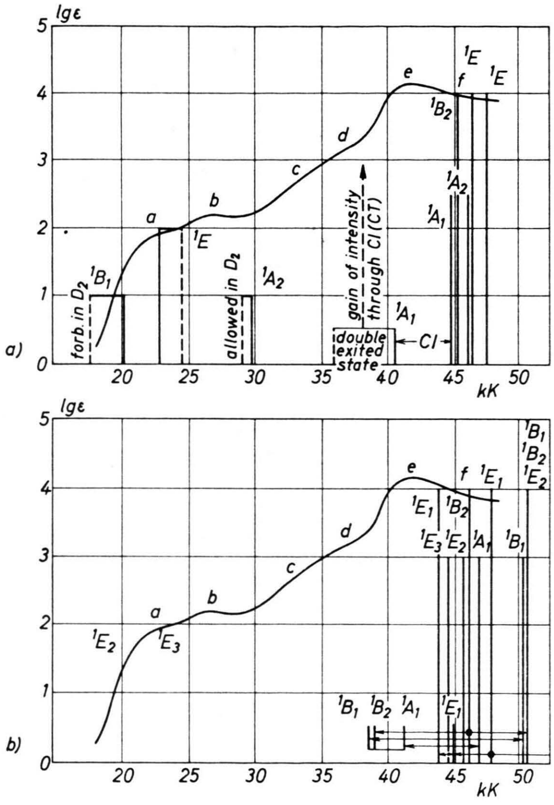

Fig. 3. Assignment of the electronic absorption spectrum of $Mo(CN)_8^{4-}$ in terms of the dodecahedral (Fig. 3 a) and the antiprismatic (Fig. 3 b) model. Assignment of excited states for the dodecahedral model: $(3b_1 \rightarrow 5a_1)$ $^1B_1$, $(3b_1 \rightarrow 7e)$ $^1E$, $(3b_1 \rightarrow 5b_2)$ $^1A_2$, $(3b_1^2 \rightarrow 5a_1^2)$ $^1A_1$, $(3b_1 \rightarrow 4b_1)$ $^1A_1$, $(3b_1 \rightarrow 3a_2)$ $^1B_2$, $(3b_1 \rightarrow 6b_2)$ $^1A_2$, $(3b_1 \rightarrow 8e)$ $^1E$; transitions drawn with a full line refer to the experimental Hoard and Nordsieck model and those drawn with a broken line refer to the hard sphere model. (The segments of the ordinates at kK=20 and kK=25 from $\lg \varepsilon = 0$ to the curve should be also full lines.)

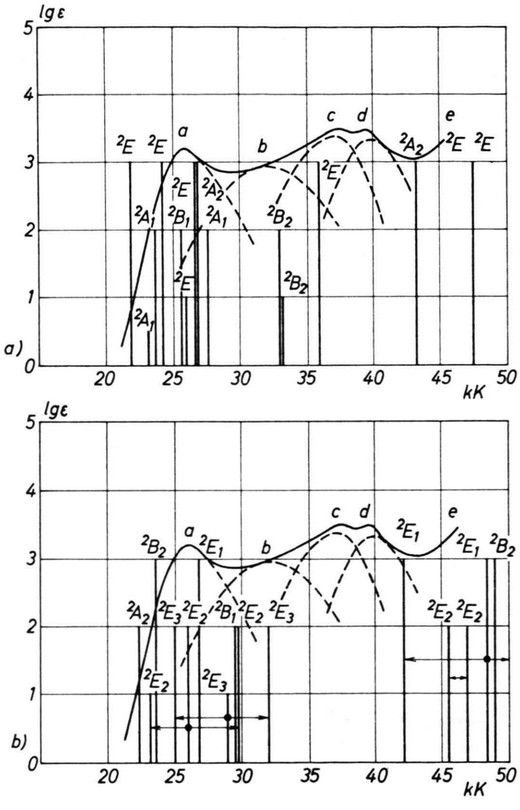

Fig. 4. Interpretation of the electronic absorption spectrum of $Mo(CN)_8^{3-}$ in terms of the dodecahedral (Fig. 4 a) and the antiprismatic (Fig. 4 b) model. Assignment of the excited states for the dodecahedral model: $(6e \rightarrow 3b_1)$ $^2E$, $(3b_1 \rightarrow 5a_1)$ $^2A_1$, $(4a_1 \rightarrow 3b_1)$ $^2A_1$, $(5e \rightarrow 3b_1)$ $^2E$, $(2b_1 \rightarrow 3b_1)$ $^2B_1$, $(3b_1 \rightarrow 7e)$ $^2E$, $(4e \rightarrow 3b_1)$ $^2E$, $(2a_2 \rightarrow 3b_1)$ $^2A_2$, $(3a_1 \rightarrow 3b_1)$ $^2A_1$, $(3b_2 \rightarrow 3b_1)$ $^2B_2$, $(3b_1 \rightarrow 5b_2)$ $^2B_2$, $(3e \rightarrow 3b_1)$ $^2E$, $(1a_2 \rightarrow 3b_1)$ $^2A_2$. Figure 4 b is redrawn from Ref. [27],

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# Absorption and Fluorescence Measurements in Compensated Cholesteric Mesophases

## Part I: Orientation of Chromophores in Liquid Crystal Solvents

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A mixture of cholesteric compounds of opposite helical twisting power at a definite temperature $T_n$ gets nematic properties because the long molecular axes take a parallel arrangement. If the sample is placed between lecithin-treated quartz plates the long axes at $T_n$ switch by an angle of 90° into a direction normal to the cover surfaces. As the orientation of the cholesteric molecules is transferred to the anisotropic solute molecules this effect has been detected by means of measurement of absorptivity and fluorescence efficiency of soluted chromophores. By the method described a possibility opens to determine the direction of optical transitions by a very simple technique.

## 1. Introduction

It is well known that in nematic liquid crystals the long axes of the molecules adhere in a parallel orientation to the supporting surface (homogeneous texture) when the cover plates had been rubbed before [1]. The same holds for molecules within a cholesteric mesophase of so-called “disturbed texture” [2]. In nematics however, the long axes adopt an orientation perpendicular to the surface of the substrate (homeotropic texture) when the plates are treated with lecithin [3]. A liquid crystal of nematic properties can be obtained at a specific temperature $T_n$ by mixing two cholesterics of opposite helical twisting power in a definite ratio of mixture (compensated cholesteric mixture) [4]. The question arises if the orientation of the molecular axes referred above is obtained in a compensated mixture at $T_n$ on treating the substrate with lecithin. That implies an overturn of the long axes from a parallel to a normal position with respect to the surface.

As in cholesteric and nematic solvents rodlike non-mesomorphic molecules on an average tend to align with their long axes in a parallel fashion with respect to those of the solvent molecules [5, 6], a change of orientation is expected also to apply to solute molecules. If chromophoric molecules are used as a solute the temperature dependence of orientation might be observed by means of absorption and fluorescence measurements, respectively. The results are checked by polarisation microscopy.

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